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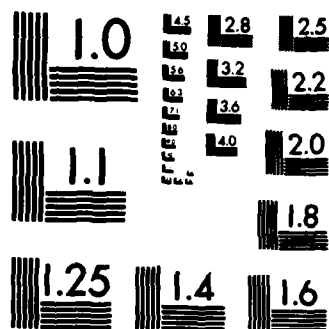| REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM	
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The goal of this program is to establish the defect chemistry of compounds whose applicability depends on the types and amounts of ionic and electronic defects. Attention was focused in this project on $LiNbO_3$, a material being studied for a variety of electro-optic device applications. The main experimental approach was the measurement of the equilibrium electrical conductivity of $LiNbO_3$ single crystals as a function of temperature (900-1100°C), oxygen partial pressure ($10^{-15} - 10^5$ Pa or $10^{-20} - 1$ atm), Li/Nb ratio (0.92-1.00),

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and impurity additions (up to 8.9 mole % MgO and 5.7 mole % TiO_2). The conductivity was characterized by an electronic component that varied as $P_{O_2}^{-1/4}$ for $P_{O_2} < 10$ Pa, and an ionic contribution tending toward P_{O_2} independence at higher P_{O_2}. Both components increased slightly (less than double) with increasing Li_2O-deficiency, but were virtually unaffected by impurity additions. The crystal density increased on reduction proving that oxygen vacancies are not the major product of reduction, as commonly assumed.

A defect model is proposed that involves only electrons, lithium vacancies, and excess niobium defects. The major conclusion is that $LiNbO_3$ has a very large degree of intrinsic ionic disorder, amounting to several percent above $900°C$, and that this controls the defect chemistry except for the most extreme limits of Li_2O-deficiency or reduction.

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Composition and Electrical Property Relationships in
Polycrystalline Inorganic Materials

AFOSR-78-3505

FINAL REPORT

Period: December 1, 1977 to October 31, 1982

PROJECTOR DIRECTOR:

Donald M. Smyth
Professor of Metallurgy and Materials Engineering
and of Chemistry

Materials Research Center
Lehigh University
Bethlehem, PA 18015

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I. INTRODUCTION

Lithium niobate, $LiNbO_3$, is a ferroelectric and electro-optic material of increasing importance and application. Early interest in $LiNbO_3$ centered around its potential applications for surface acoustic wave propagation, electro-optic modulation, parametric amplification, and phase-matched optical second harmonic generation (1). It was also considered as a laser host crystal for Cr^{+3} and Nd^{+3} ions (2-4). One problem with the use of $LiNbO_3$ in these applications was its susceptibility to optical damage (the photorefractive effect) when irradiated with visible light. The photorefractive effect causes localized inhomogeneities in the refractive index of the crystal, inducing a decrease in the extraordinary index by as much as 10^{-3} (5,6). Coherent light from a laser beam diverges under these conditions, and it was thought that fabrication of a reliable electro-optic device was impractical. It was determined that this effect was caused by defect centers and impurity ions (chiefly Fe) in the crystals (7-9). It was also found that the crystal stoichiometry has a major effect on the susceptibility to optical damage (10-12). In fact, the photorefractive effect proved a boon when it was learned that phase holograms, suitable for optical information storage, could be generated in the material (13,14).

Currently, optical waveguides prepared by transition metal in-diffusion or by Li_2O out-diffusion on a single crystal $LiNbO_3$ substrate are being used in the fabrication of integrated optical devices. Devices successfully demonstrated in single mode operation include multiplexers and de-multiplexers and polarization insensitive electro-optic switches, filters, couplers and modulators (15). Projected applications include a multi-mode electro-optic switch to be used in a submarine cable light-wave system (15).

1.

Many of the critical properties of $LiNbO_3$ are clearly dependent on lattice defects and electronic disorder, and hence on deviations from stoichiometry and the presence of impurities. This program was designed to carry out a systematic study of the defect chemistry of $LiNbO_3$ with the goal of achieving a self-consistent defect model. It was clear from the available literature that the situation was confused and contradictory at that time.

The major experimental technique has been the measurement of the equilibrium electrical conductivity as a function of temperature (800-1100°C), oxygen partial pressure (10^{-18}-1 atm), Li/Nb ratio, and impurity additions. These results have been supplemented by a parallel study of the mechanism and kinetics of diffusion of Ti into $LiNbO_3$, carried out by Dr. Ronald J. Holmes, a Member of the Technical Staff, Bell Laboratories, Allentown, and at that time a Ph.D. candidate at Lehigh working with the Principal Investigator. The work of Mr. Holmes was fully supported by Bell, and our program also benefited from the availability of samples and preparative procedures associated with his dissertation research.
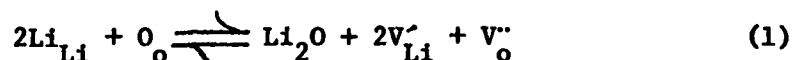
II. PREVIOUS WORK ON $LiNbO_3$

For $LiNbO_3$, a ternary oxide, the phase rule specifies that in addition to temperature and total pressure, the activities of two components must be specified to complete a thermodynamic description of the system. The oxygen partial pressure, P_{O_2}, is one natural candidate, and in this case it is convenient to identify the activity of Li_2O as the other. Thus we can consider two types of nonstoichiometry, the ratio of oxygen to the total metal content, and the ratios of the two metallic constituents, Li and Nb. P_{O_2} is a convenient experimental variable, and Holman has shown
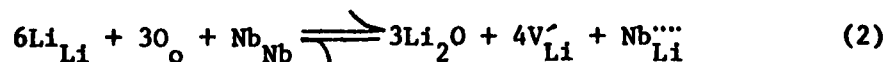
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that the Li_2O content can be adjusted within reasonable times by close exposure to active sources or sinks of Li_2O at elevated temperatures (16). In the absence of a source or sink, the Li_2O content of $LiNbO_3$ changes very sluggishly, especially in near-stagnant gas-flow conditions. This fortunate set of circumstances allows the measurement of the physical properties of $LiNbO_3$ as a function of temperature and P_{O_2} at constant Li_2O content across the entire phase field of the compound.

It has long been recognized that the $LiNbO_3$ phase field extends to substantial deficiencies of Li_2O (17), the location of the phase boundary has varied with experimental technique, but the thermogravimetric work of Holman (16), precisely confirmed by Holmes (18), gives the definitive result, based on the sole assumption that the Li_2O-rich phase boundary occurs at 50.00 mol % Li_2O. This assumption, which implies that there are no Li_2O-rich compositions, has been supported by Holman on the basis of Knudsen effusion and thermogravimetric measurements previously used for the $PbTiO_3$-$PbZrO_3$ system (19).

Fay, Alford, and Dess (20) proposed that Li_2O loss proceeds by the reaction

$$2Li_{Li} + O_o \rightleftharpoons Li_2O + 2V'_{Li} + V_o^{\cdot\cdot}$$ (1)

This implies the conservation of lattice sites, the Li_2O merely leaving behind their vacant lattice sites. Lerner, Legras, and Duman subsequently found, however, that the density of $LiNbO_3$ _increases_ with Li_2O loss, whereas Eq. (1) would require a decrease (17). These authors therefore proposed that unit cells are lost in proper stoichiometric ratio as the Li_2O content decreases and proposed the reaction
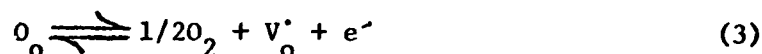
$$6Li_{Li} + 3O_o + Nb_{Nb} \rightleftharpoons 3Li_2O + 4V'_{Li} + Nb_{Li}^{\cdots\cdots}$$ (2)

3.

the Nb left-over by the loss of unit cells moving into the crystal and substituting for some of the missing Li. $Nb_{Li}^{....}$ was preferred over $Nb_I^{.....}$ on the basis of the amount of excess charge. Nassau and Lines confirmed the density measurement, but suggested a local rearrangement around the excess Nb in the form of a stacking fault, in order to give better separation of the Nb atoms (21).

The defect structure of Li_2O-deficient $LiNbO_3$ is of major practical importance because commercially available single crystals are grown from the congruently melting composition, which corresponds to 48.6 mol % Li_2O. This is, in fact, not far from the Li_2O-deficient phase boundary, and, on the basis of Eq. (2) corresponds to 3.66% of the Li sites being vacant, and 0.92% of them containing Nb. These are very large defect concentrations. This composition is also metastable below 800°C, and it must be cooled rapidly to avoid phase separation.

Both Bergmann (22) and Jorgensen and Bartlett (23) studied the oxygen nonstoichiometry by measurement of the equilibrium electrical conductivity as a function of P_{O_2} and temperature. It appears that their single crystals were of the congruent composition. Their results are shown in Figure 1. Both found that the conductivity varied as $P_{O_2}^{-1/4}$ for P_{O_2} less than about 10^{-5} atm in the temperature range 730–1150°C, and attributed this to n-type electronic conduction. The conductivity became less dependent on P_{O_2} at higher partial pressures, and appeared to be increasingly ionic in nature. Joregnsen and Bartlett observed that the ionic component of conductivity increased when a boat of Li_2O was placed below the sample, but that the electronic part was unaffected.

4.

Both groups attributed the n-type conduction to oxygen-loss with the formation of singly-ionized oxygen vacancies

$$O_o \rightleftharpoons 1/2O_2 + V_o^{\cdot} + e^{\prime} \qquad (3)$$

If this reaction is the major source of both $V_o^{\cdot}$ and $e^{\prime}$, then

$$[V_o^{\cdot}] \sim n \qquad (4)$$
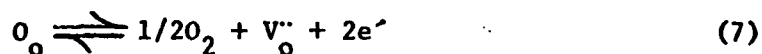
and with the mass action expression for Eq (3)

$$[V_o^{\cdot}]n = K_3 P_{O_2}^{-1/2} \qquad (5)$$

one obtains

$$n \sim [V_o^{\cdot}] \sim K_3^{1/2} P_{O_2}^{-1/4} \qquad (6)$$

The ionic conduction was attributed to Li ions (23) or to Frenkel defects (22).

Jarzebski has pointed out that the $P_{O_2}^{-1/4}$ dependence of electronic conductivity can also be obtained with doubly-ionized oxygen vacancies if the vacancy concentration is essentially independent of P_{O_2}, e.g. if it is fixed by the impurity content (24). Thus for the reaction

$$O_o \rightleftharpoons 1/2O_2 + V_o^{\cdot\cdot} + 2e^{\prime} \qquad (7)$$

with

$$[V_o^{\cdot\cdot}] \neq f(P_{O_2}) \qquad (8)$$

then the mass action expression

$$[V_o^{\cdot\cdot}]n^2 = K_7 P_{O_2}^{-1/2} \qquad (9)$$

gives

$$n \propto P_{O_2}^{-1/4} \qquad (10)$$

Although the oxygen vacancy model for reduced LiNbO$_3$ has been universally accepted, it is almost certainly incorrect. On general principles it is

5.

inconsistent to propose one set of defects for Li_2O-deficiency, and a different set for oxygen loss. There must be continuity in the defect model. The defect diagram can be viewed as three-dimensional with defect concentrations as the ordinate and the Li_2O and O activities as mutually perpendicular abscissae. The defect concentrations must vary smoothly with the activities in all directions as long as there is no phase change. Since the change of density with Li_2O-loss excludes the oxygen vacancy mechanism, Eq (1), it should not be expected for oxygen-loss. In fact we have subsequently determined that the density also increases when a crystal of the congruent composition is reduced. This makes the oxygen vacancy model of reduction completely untenable.

III. EXPERIMENTAL

Undoped crystals of $LiNbO_3$ were obtained from Crystal Technology. Collaboration with Professor Robert Feigelson of the Center for Materials Research at Stanford University, supported by sub-contract from this grant, led to the availability of several doped crystals. More highly doped crystals have been generously donated by Bell Laboratories. Conductivity specimens in the form of thin bars, approximately 1.8x0.25x0.05 cm, were cut by a slow-speed diamond saw. Platinum wires, 0.025 cm in diameter, were wrapped around the bars to give four electrodes for the 4-point, AC technique. The data were accumulated by a Keithley System 76 data acquisition system that measured the voltages of all the thermocouples, the emf of the O_2-activity cell, and the voltage drops across a standard resistor and the experimental samples (up to three sa les cou' be accommodated at the same time). The data were processed by the system and printed out as temperatures, P_{O_2}, and the conductivities of the samples. The

6.

measurements were made at a frequency of 1000 hz. A reactive component of the conductivity appeared in the region of significant ionic conduction; only the resistive component is shown in the figures.

The Li_2O content of the crystals was adjusted by the vapor phase equilibration technique of Holman (16), i.e. the sample was enclosed in a volume surrounded by a two phase mixture of either Li_3NbO_4 and $LiNbO_3$ (Li_2O source), or $LiNb_3O_8$ and $LiNbO_3$ (Li_2O sink). These mixtures fix the Li_2O activity at the appropriate phase boundary, and the thin conductivity samples will shift to the desired phase boundary composition over a period of the order of 100 hours in the vicinity of 1000°C. The process of equili-bration can be followed by thermogravimetry. In the absence of an active source or sink for Li_2O in very close proximity, the crystals do not change composition even after days of conductivity measurements in a slow gas flow in the 900-1100°C range. This extremely fortunate situation obviates the need for simultaneous equilibration with O_2 and Li_2O during the conductivity measurement. It should be noted that this technique fixes the Li_2O content (or Li/Nb ratio) in the sample rather than the Li_2O activity except, of course, at the temperature used for the equilibra-tion. Considerable effort was expended in attempts to include Li_2O equilibration into the conductivity furnace, but the extremely corrosive nature of hot Li_2O vapor, and the slow rate of equilibration, eventually led to abandonment of this ideal situation.

The oxygen activity was determined by metered mixtures of $Ar-O_2$ and $CO-CO_2$. The oxygen activity was measured adjacent to the conductivity samples by means of an oxygen concentration cell using a closed-end CaO-doped ZrO_2 tube with pure O_2 as the reference.

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IV. RESULTS AND DISCUSSION
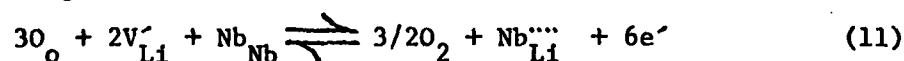
A. CONGRUENT LiNbO$_3$

Results of our measurements of the electrical conductivity of congruent LiNbO$_3$ as a function of temperature and P$_{O_2}$ are shown in Figure 2. The results are similar to those of Bergmann (22) and of Jorgensen and Bartlett (23), although the curvature at high P$_{O_2}$ and the parallel nature of the isotherms are displayed more clearly. The dependence of conductivity on P$_{O_2}^{-1/4}$ at low P$_{O_2}$ is confirmed. Concentration cell measurements by Jorgensen and Bartlett indicated predominantly electronic conduction in this region with increasing ionic conduction appearing as the P$_{O_2}$ dependence decreases at high P$_{O_2}$. This is in accord with the observation of an increasing reactive component of the impedence in this region in our AC measurements.

In principle, the P$_{O_2}^{-1/4}$ dependence can occur in two different ways. It will always result when reduction leaves two mobile electrons in the crystal for each oxygen atom lost and there is no significant change in concentration of the ionic defects created by reduction, i.e. when the major source of ionic defects is due to impurities, to the deviation from the ideal Li/Nb ratio, or to intrinsic ionic disorder. This corresponds to the case of complete ionization of the defects. An alternative mechanism leading to this dependence involves only partial ionization of some of the defects, or stated differently, some of the electrons resulting from reduction are trapped so that there are less than two mobile electrons per oxygen atom lost. In this case the reduction reaction must be the major source of one or more ionic defects. By itself, the P$_{O_2}^{-1/4}$ dependence cannot distinguish between these two possibilities, nor does

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it give any additional atomistic information. As will be seen, the former situation involving completely ionized defects is in better agreement with our results, rather than the model involving partially ionized oxygen vacancies proposed by Bergmann (22) and by Jorgensen and Bartlett (23).

The density measurements of Lerner et al. indicate that Li_2O loss does not occur by the simple subtractive mechanism of Eq. (1) (17). Nassau and Lines found that the density of a crystal of congruent composition 48.6 mol % Li_2O is in excellent agreement with the calculated value if a full oxygen sublattice is maintained (21). This has been confirmed by Holmes (25). Thus for each $3Li_2O$ lost from the crystal, a set of $LiNbO_3$ lattice sites are lost. Again, no further atomistic information is given. Lerner et al. (17) suggested a Li_2O-loss reaction of the type shown in Eq. (2). Of the six Li sites vacated, one site is lost, and another is occupied by the Nb that is displaced from its lost lattice site. $Nb_{Li}^{\cdots\cdots}$ + $4V_{Li}'$ was chosen instead of $Nb_I^{\cdots\cdots}+5V_{Li}'$ to minimize the charge on the Nb defect. A simple calculation based on Eq. (2) shows that congruent $LiNbO_3$, containing 48.6 mol % Li_2O, would have 3.66% $[V_{Li}']$ and 0.92% $[Nb_{Li}^{\cdots\cdots}]$. With these very high defect concentrations, one would not expect the concentrations of ionic defects to be significantly affected by modest degrees of reduction.

Based on this model for Li_2O-loss, one would not expect reduction to result in the formation of oxygen vacancies. This has been confirmed by the observation of Holmes that the density of a congruent crystal increases on reduction (24). Thus a reasonable and consistent reduction reaction for Li_2O-deficient $LiNbO_3$ would be

$$3O_o + 2V_{Li}' + Nb_{Nb} \rightleftharpoons 3/2O_2 + Nb_{Li}^{\cdots\cdots} + 6e' \qquad (11)$$

9.

with the corresponding mass action expression

$$\frac{[Nb_{Li}^{....}]n^6}{[V_{Li}^{'}]^2} = K_{11}P_{O_2}^{-3/2} \tag{12}$$

If the ionic defects are due primarily to Li_2O deficiency then

$$[V_{Li}^{'}] \underset{\sim}{\sim} 4[Nb_{Li}^{....}] \tag{13}$$

and

$$n \underset{\sim}{\sim} (4K_{11})^{1/6}[V_{Li}^{'}]^{1/6}P_{O_2}^{-1/4} \tag{14}$$

in agreement with the observed P_{O_2} dependence. This requires that all of the electrons generated by reduction contribute to the conductivity, i.e. the defects are fully ionized as shown. The results give no further information on the mechanism of conduction.

Arrhenius plots of the conductivity at constant P_{O_2} are shown in Figure 3. The slopes correspond to activation energies of 241 kJ/mol (2.50 eV).

Holmes measured a weight loss of 0.0326±0.0015% for two congruent samples reduced at 1050°C in 10^{-12} atm of O_2 (25). This corresponds to $[Nb_{Li}^{....}] = 0.1$ mol % and $n = 0.6$ mol % or 1.13×10^{26} m^{-3}. Combined with our conductivity data, this gives an electron mobility at this temperature of $1.9 \times 10^{-6} m^2/v$ sec, a magnitude that suggests some sort of hopping mechanism. Nagels has analyzed the conduction mechanism of reduced $LiNbO_3$ by a combination of conductivity, thermoforce, and Hall measurements up to about 500°C (26). He found an extremely good fit with small polaron theory with a drift mobility of the form

$$\mu_n \propto T^{-3/2}e^{E_n/kT} \tag{15}$$

with $E_n = 0.49$ eV. Extrapolation of his results to 1050°C gives $\mu_n = 1.8 \times 10^{-6}$ m^2/v sec, in extraordinarily good agreement with our result. Our calculation was based on the assumption of complete defect ionization, which is thus supported.

10.

The conductivity can then be expressed as

$$\sigma \propto T^{-3/2} e^{-\left(\frac{\Delta H_{11}}{6} + E_n\right)/kT} \tag{16}$$

where ΔH_n is the enthalpy of the reduction reaction, Eq. (11). From the data of Figure 3, this gives $\Delta H_{11} = 1248$ kj/mole or 208 kj/mole per electron (2.16 eV per electron). This is significantly less than the value of 2.95 eV per electron found for $BaTiO_3$ and $SrTiO_3$ (27,28). This indicates a greater ease of reduction for the niobate.

Nagels found not only a thermally activated drift mobility, but also a thermally activated carrier concentration up to 500°C, with an activation energy of 0.25 eV. This implies that the electrons are localized in a deep trap from which they are thermally ionized to a conducting but still localized state that has a mobility with an activation energy of 0.49 eV. From our conductivity results and the extrapolated μ_n of Nagels, the calculated carrier concentration at the temperature and P_{O_2} used by Nagels to reduce his samples is very close to the maximum value shown by him at 500°C. The donor traps must thus be nearly ionized at the latter temperature. The identity of the trap is not clear. It could possible be $Nb_{Li}^{\cdots\cdots}$ since the charge on this defect would be reduced by the trapping of an electron. The ionization step might then be

$$Nb_{Li}^{\cdots\cdots} + Nb_{Nb} \rightleftharpoons Nb_{Li}^{\cdots\cdots} + Nb_{Nb}' \tag{17}$$

Conduction could then occur by hopping on the Nb sublattice.

B. THE EFFECT OF VARIATIONS IN Li/Nb

Conductivities of samples equilibrated to the Li_2O-rich and Li_2O-deficient phase boundaries at 1050°C are shown in Figure 4, along with comparable data on the congruent composition. The conductivity increases

11.

with increasing Li_2O-deficiency, as predicted by Eq. (14). This is contrary to the report of Jorgensen and Bartlett who observed an increase in conductivity in the region of high P_{O_2} when a boat of Li_2O was placed beneath the $LiNbO_3$ sample during the conductivity measurement (23). Exposure to Li_2O had no effect on the conductivity in the region of electronic conduction, however. We found that $LiNbO_3$ was transformed into a polycrystalline mass when exposed to Li_2O held at 200°C less than the $LiNbO_3$ crystal. Clearly the Li_2O activity has exceeded that included in the stability range of $LiNbO_3$ and conductivity measurements made under such circumstances are invalid. The Holman technique for adjusting the composition avoids that problem (16).
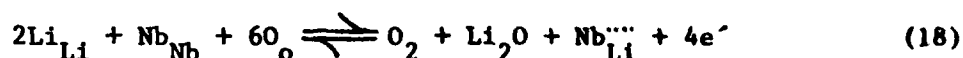
According to the Li_2O-deficient phase boundary determined by Holman (16) and Holmes (18), the defect concentration in the Li_2O-deficient sample exceeds that of the congruent composition by only about 35%, so it is not surprising that its conductivity profile is only slightly higher. The major surprise is that the Li_2O-rich sample has a conductivity that is less than that of the congruent sample by such a small factor.

Holman found that the Li_2O-rich phase boundary was indistinguishable from Li/Nb=1.000 (16). Holmes measured the density of a Li_2O-rich sample to be 4.620 g/cm^3 which compares well with the calculated ideal density of 4.625 g/cm^3 (25). (The measured density of congruent crystals was 4.649 g/cm^3.) Both pieces of evidence indicate that Li_2O-rich $LiNbO_3$ corresponds closely to the ideal Li/Nb ratio and that the concentration of defects related to Li/Nb nonstoichiometry should be much less than that of congruent and Li_2O-deficient crystals. Yet the behavior of all of the samples is surprisingly similar in both magnitude and form, and even in temperature dependence. If the defect concentration due to Li_2O-loss were small

12.

compared to the amount of reduction, then Eq. (13) would no longer be valid, since all of the V_{Li}' would be consumed by even modest degrees of reduction. It is thus difficult to ascribe the $P_{O_2}^{-1/4}$ dependence of the conductivity of Li_2O-rich samples to a model involving fully ionized defects with the ionic defect concentration fixed by nonstoichiometry in the Li/Nb ratio.
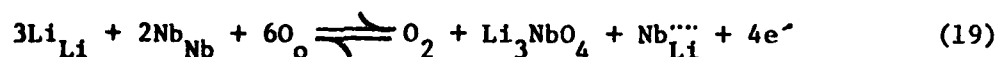
When Li_2O-deficient, congruent, and Li_2O-rich samples have been subjected to strongly reducing atmospheres in the course of the conductivity measurements and have then been reoxidized and cooled, it was observed that the Li_2O-rich sample was cloudy whereas the other two compositions remained clear. Comparison of the proposed Li_2O-loss and reduction reaction shows that reduction changes the defect concentrations in such a way as to increase the effective activity of Li_2O. Since the Li_2O-rich samples are already saturated with Li_2O, it is to be expected that reduction will ultimately cause the separation of a second phase of higher Li_2O content, i.e. Li_3NbO_4. The principles involved in this situation have been discussed previously (29).

The overall reduction situation can be summed up by the general equation

$$2Li_{Li} + Nb_{Nb} + 6O_O \rightleftharpoons O_2 + Li_2O + Nb_{Li}^{\cdots\cdots} + 4e'$$
(18)

This equation makes no assumptions about the original state of stoichiometry of the material since no defects are consumed. It retains a full oxygen sublattice as indicated by the density measurements and assumes that $Nb_{Li}^{\cdots\cdots}$ is favored over $Nb_I^{\cdots\cdots} + V_{Li}'$. Otherwise it is perfectly general. If the starting material is sufficiently Li_2O-deficient, then the Li_2O produced by reduction as shown in Eq. (18) can redissolve in the $LiNbO_3$ according to the reverse of Eq. (2), raising the Li/Nb ratio, and giving Eq. (11) as the overall reaction. If the crystal is already saturated with Li_2O, the

13.

additional Li_2O will combine with $LiNbO_3$ to give the adjacent Li_2O-rich phase

$$3Li_{Li} + 2Nb_{Nb} + 6O_o \rightleftharpoons O_2 + Li_3NbO_4 + Nb_{Li}^{\cdots} + 4e' \qquad (19)$$

with the mass-action expression

$$[Nb_{Li}^{\cdots}]n^4 = K_{19}a_L^{-1}P_{O_2}^{-1} \qquad (20)$$

The separation into two phases fixes the Li_2O activity, a_L, at the phase boundary value. If Eq. (19) is the major source of defects then

$$n \approx 4[Nb_{Li}^{\cdots}] \qquad (21)$$

and

$$n \propto K^{1/5} a_L^{-} P_{O_2}^{-1/5} \qquad (22)$$

which does not agree with the observed dependence of conductivity on P_{O_2}. If there is another dominant source of $Nb_{Li}^{\cdots}$, then the dependence is as observed

$$n \propto \left\{\frac{K_{19}}{[Nb_{Li}^{\cdots}]}\right\}^{1/4} a_L^{-1/4} P_{O_2}^{-1/4} \qquad (23)$$

The similarity in behavior of the conductivity of the Li_2O-rich samples with those of the other compositions, including the activation energies, suggests that the material can become extensively supersaturated with Li_2O before phase separation occurs. In other words, the Li_2O-rich material reduces extensively according to Eq. (11) until the supersaturation is sufficient to cause nucleation of the second phase. During this period prior to phase separation, the mechanism is very similar to that of Li_2O-deficient material. The source of V_{Li}' required for Eq. (11) will be discussed in a later section.

14.

C. THE BEHAVIOR AT VERY LOW P_{O_2}

The results shown so far have extended down to only about 10^{-10} atm oxygen. This is partly because this is sufficient to demonstrate the dependence of conductivity on P_{O_2}, but, more importantly, it is because of "peculiar" behavior at lower P_{O_2}. For $P_{O_2} < 10^{-14}$ atm equilibration becomes very sluggish, taking hours instead of a few minutes. Reversibility is also retarded; if the P_{O_2} is returned to 1 atm after an extended period at very low P_{O_2}, the conductivity is higher than originally at 1 atm and the return to the previous value is very slow. A new phenomenon has clearly come into play in the region of very low P_{O_2}. It is difficult to determine a precise P_{O_2} dependence of the conductivity at very low P_{O_2} because of the slow equilibration and poor reversibility, but the trend seems similar to the $P_{O_2}^{-1/4}$ dependence observed at higher P_{O_2}.

This behavior is attributed to nucleation and separation of the adjacent Li_2O-rich phase, Li_3NbO_4. For Li_2O-deficient material, reduction consumes $2V_{Li}'$ for each $Nb_{Li}^{\cdots}$ generated as shown in Eq. (11). From the mass-action expression for the Li_2O-loss reaction, Eq. (2),

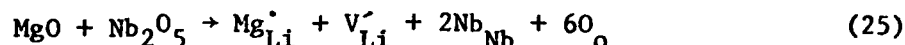$$[Nb_{Li}^{\cdots}][V_{Li}']^4 = K_2 \, a_L^{-3} \qquad (24)$$

the net effect of this reduction is to decrease the left-hand-side which requires an increase in a_L to maintain the equality. a_L is thus driven toward the Li_2O-rich phase boundary by reduction. It is proposed that the samples reach the phase boundary and achieve a sufficient degree of super-saturation to nucleate a second phase at about $P_{O_2} \sim 10^{-14}$ atm at 1000°C. This suggests a three-dimensional phase diagram with a cross-section at constant temperature as shown in Fig. 5. This is highly schematic, but the relative slopes of the lines are drawn in accord with the above model.

15.

When the highly reduced, phase-separated samples are reoxidized, the Li_2O-deficient samples become clear and transparent, because they are returned to a position deep within the single phase region while the Li_2O-rich sample remains cloudy. Evidence for the presence of second phase in highly reduced, Li_2O-deficient $LiNbO_3$ is currently being sought.

D. IMPURITY ADDITIONS

The addition of aliovalent impurities can give important information about the defect structure if the result is a significant change in defect concentrations. This will cause systematic changes in the equilibrium electrical conductivity by interaction through the corresponding mass-action expression. We have obtained doped $LiNbO_3$ crystals from Crystal Technology, by means of a collaborative effort with Professor Robert Feigelson of the Center for Materials Research of Stanford, supported by sub-contract from this grant, and as donations from Bell Laboratories. Crystals containing about 0.08 and 0.8 mol % MgO, obtained from Professor Feigelson, were indistinguishable from undoped crystals in terms of equilibrium conductivity, regardless of whether the crystals were congruent, Li_2O-deficient, or Li_2O-rich. We expect to receive crystals from the same source doped with Al and Mo at higher levels. In the meantime, we have examined as-grown (congruent) and Li_2O-rich compositions of samples with 8.9 mole % MgO and 5.7 mole % TiO_2, furnished by Bell Laboratories. These very high impurity levels also had no significant effect on the equilibrium conductivity. This persistent inertness to doping effects was unanticipated.

Incorporation of MgO during crystal growth from the melt would be expected to proceed according to the equation

16.

$$MgO + Nb_2O_5 \rightarrow Mg_{Li}^{\cdot} + V_{Li}^{'} + 2Nb_{Nb} + 6O_o \qquad (25)$$

Mg^{++} should substitute for Li^{+} because of the small charge differential. The 8.9 mole % MgO should have generated 8.9% $V_{Li}^{'}$. At the congruent composition, this would be in addition to the 3.66% due to Li_2O-deficiency. If the conductivity varies with $[V_{Li}^{'}]^{1/6}$ as predicted by Eq. (14) the conductivity of the doped sample should have been higher by 23%. Even this modest change could not be confirmed. Even more puzzling, the effect on the Li_2O-rich composition, where the dopant should have had a much larger relative effect, was no different. Similar results were obtained with the TiO_2-doped samples. These observations are an important ingredient of the defect model proposed in the next section.

V. PROPOSED DEFECT MODEL

The major information to be considered in developing a defect model for $LiNbO_3$ includes the following:

1. Changes in the Li/Nb ratio, from the near-stoichiometric Li_2O-rich phase boundary to the grossly nonstoichiometric Li_2O-deficient phase boundary, has only a small effect on both the electronic conductivity at low P_{O_2} and the increasing ionic component at high P_{O_2}. Both types of conductivity increase gradually with increasing Li_2O-deficiency.

2. Large additions of aliovalent impurities, up to 8.9 mole % MgO and 5.7 mole % TiO_2 have no discernable effect on either conductivity component at any Li/Nb ratio.

3. Typical calculated defect contributions from nonstoichiometry are 3.66% $V_{Li}^{'}$ and 0.92% $Nb_{Li}^{\cdots}$ at the congruent composition, and 0.6% $e^{'}$ (expressed as % of Nb-sites) and an additional 0.1% $Nb_{Li}^{\cdots}$ for a congruent sample reduced at 1050°C and $P_{O_2} \approx 10^{-12}$ atm.

17.

4. The electronic conductivity of all samples varies as $P_{O_2}^{-1/4}$ while the ionic component seems to be approaching P_{O_2}-independence at high P_{O_2}.

5. Comparison with the conductivity study of Nagels (26), indicates that at 900–1100°C all electrons generated by reduction are available for conduction without further activation, i.e. the ionic defects are fully ionized.

6. Reduction of Li_2O-rich samples results in visible phase-separation. For $P_{O_2} \stackrel{\sim}{<} 10^{-14}$ atm, the sluggish equilibration rates suggest phase separation for all samples.

7. The density of congruent crystals are consistent with retention of a filled oxygen sublattice. The density of Li_2O-rich samples is close to the ideal crystal density. The density of congruent crystals increases on reduction.

The density measurements indicate that oxygen vacancies are not a major product of either Li_2O-deficiency, or reduction. They are not absolutely excluded, but their concentration must be insignificant compared with the major defects. The universal assumption that oxygen vacancies are the major product of reduction is incorrect (22,23,30).
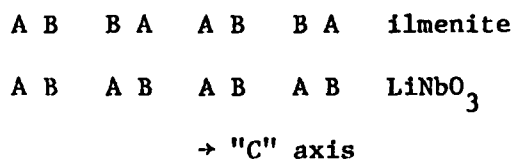
The evidence for full ionization of the defects and the dependence of the electronic conductivity on $P_{O_2}^{-1/4}$ indicates that reduction has a negligible effect on the total ionic defect content for all values of Li/Nb. There are three other major sources of ionic defects:

1. The impurity content

2. Nonstoichiometry in Li/Nb

3. Intrinsic ionic disorder

Generation of defects in the percent concentration range by reduction confirms that the background impurity content of undoped crystals is

inadequate to control the defect concentration over the full range of reduction. Likewise, the defect concentrations due to Li/Nb nonstoichiometry for samples equilibrated at the Li_2O-rich phase boundary should not exceed those generated by severe reduction. The remaining possible dominant source of ionic defects is intrinsic ionic disorder. There is insufficient evidence to prove that this is the dominant effect, but it is the only possibility that cannot be excluded with a fair degree of certainty. The evidence requires that the dominant defects be present at the level of several percent over the range 900-1100°C. This corresponds to a very highly disordered material. The following discussion will explore the plausibility of such an extraordinary degree of disorder in $LiNbO_3$.
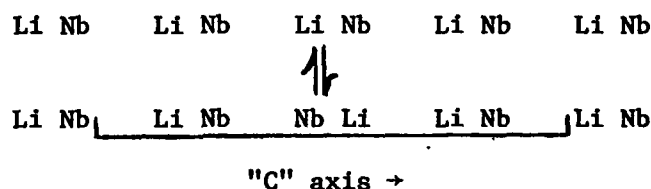
In order to consider the ease with which defects can be accommodated by a given compound, it is necessary to consider the crystal structure in some detail. The $LiNbO_3$ structure can be viewed as a variant of the corundum structure (α-Al_2O_3), similar to the ilmenite structure. All have an approximately hexagonal close-packed oxygen sublattice that results in strings of octahedral sites parallel to the hexagonal axis. 2/3 of these sites are occupied in the sequences shown in Fig. 6, taken from Wells (31). The $LiNbO_3$ and ilmenite structures, generalized as ABO_3, differ only in the cation sequence.

$$A\ B \quad B\ A \quad A\ B \quad B\ A \quad \text{ilmenite}$$

$$A\ B \quad A\ B \quad A\ B \quad A\ B \quad LiNbO_3$$
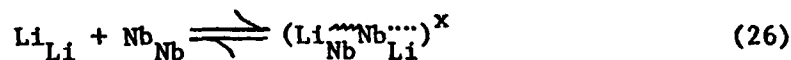
$$\rightarrow\ \text{"C" axis}$$

Apparently the higher charge on the Nb compared with Ti makes it less favorable for two cations to be in opposition across the unoccupied site in the case of $LiNbO_3$. One can wonder, however, if there is much energetic

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difference between the two packing sequences. For example, $NaSbO_3$ and $NaBiO_3$, both having a 1-5 combination of oxidation states like $LiNbO_3$, have the ilmenite structure (32). Moreover, neutron diffraction studies on ilmenite itself, $FeTiO_3$, are best fit by a 10% disordering of the cation positions (33). A number of ABO_3 having two different trivalent cations have either completely random cation distributions, or have an order-disorder reaction at elevated temperatures. Finally, two types of NMR signals from Nb have been observed for congruent $LiNbO_3$ (34). The intense signal was assumed to be related to Nb located on the proper site, while a second line, of about 6% relative intensity, was attributed to Nb located on Li sites. This intensity is too high, however, relative to the expected concentration of 1% $Nb_{Li}^{\cdots\cdots}$ if these defects are due only to Li_2O-deficiency. It could reflect a 6% intrinsic cation stacking disorder, however. This is just the concentration range of intrinsic disorder needed to fit our experimental observations.

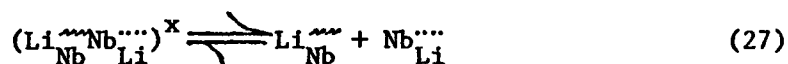One can envision the following type of intrinsic disorder:

Li Nb   Li Nb   Li Nb   Li Nb   Li Nb

Li Nb   Li Nb   Nb Li   Li Nb   Li Nb

"C" axis →

In defect notation this can be represented as the place-exchange reaction

$$Li_{Li} + Nb_{Nb} \rightleftharpoons (Li_{Nb}^{\sim\sim\sim}Nb_{Li}^{\cdots\cdots})^{x} \qquad (26)$$

The product is shown in parentheses to indicate that it is in effect a defect complex of net neutral charge (indicated by superscript x), bound on adjacent octahedral sites by electrostatic attraction. Note that exchange of a single pair of cations results in transformation of the indicated line segment, containing ten octahedral sites, into the ilmenite

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stacking sequence. If two pair exchange places with a single unchanged

pair between them, the ilmenite sequence extends for 16 octahedral sites.

If nearby pairs in adjacent strings of octahedral sites also exchange

places, then a coherent volume element of ilmenite structure would result.

This suggests the possibility of ilmenite domains in the $LiNbO_3$ structure,

a gradual transition from thermally activated disorder to phase separation.
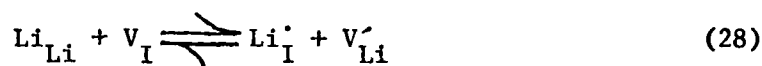
The disorder exemplified by Eq. (26) is still inadequate because

$(Li_{Nb}^{'''}Nb_{Li}^{''''})^x$ is an identifiable species distinct from the $Nb_{Li}^{''''}$ postulated

to result from reduction. If reduction does not significantly affect

the concentration of $Nb_{Li}^{''''}$, then the intrinsic disorder complex must be

extensively dissociated to given individual, randomly distributed point

defects

$$(Li_{Nb}^{'''}Nb_{Li}^{''''})^x \rightleftharpoons Li_{Nb}^{'''} + Nb_{Li}^{''''} \qquad (27)$$
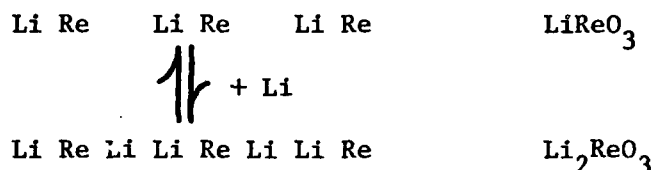
It is not unlikely that in a highly polarizable, ferroelectric material

such as $LiNbO_3$, the electrostatic attraction between oppositely charged

defects is greatly reduced. An alternative picture would be for the

$Nb_{Li}^{''''}$ generated by reduction to be incorporated into or added onto coherent

domains of ilmenite structure in a way that does not change the defect

content of the $LiNbO_3$ matrix.

The very substantial level of ionic conductivity observed in $LiNbO_3$

suggests a high degree of Li disorder. The increase in ionic conducti-

vity with increasing Li_2O-deficiency indicates that the likely mobile

species is V_{Li}'. The small change in ionic conductivity across the full

range of Li/Nb ratio implies that the total concentration of mobile

ionic carriers is not changing much and that even the Li_2O-rich composition

must have a substantial concentration of Li defects. This is consistent
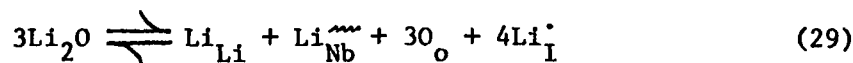
with a high degree of Li Frenkel disorder

$$Li_{Li} + V_I \rightleftharpoons Li_I^{\cdot} + V_{Li}^{'} \tag{28}$$

where V_I is the normally vacant octahedral (interstitial) site. $V_{Li}^{'}$ seems to be an inescapable element of the large extent of Li_2O-deficiency that can be achieved and is thus easily tolerated by the structure. Evidence for the ease of formation of $Li_I^{\cdot}$ can be seen in the transformation of $LiReO_3$, which has the $LiNbO_3$ structure, into Li_2ReO_3 by the addition of Li (35). This is achieved by filling the normally empty octahedral sites, the interstitial sites, with Li^+ while reducing Re^{+5} to Re^{+4}

Li Re   Li Re   Li Re $LiReO_3$

⇅ + Li

Li Re Li Li Re Li Li Re Li_2ReO_3

Li_2ReO_3 is then a variation of the NiAs structure.

A high degree of Li Frenkel disorder offers a mechanism whereby Li_2O-rich $LiNbO_3$ can reduce by the same mechanism as Li_2O-deficient material by retaining the excess Li_2O formed by reduction, Eq. (18), in supersaturated solid solution. The net effect could be that of Eq. (11) with the $V_{Li}^{'}$ originating from the Frenkel disorder. As the incorporated Li_2O consumes $V_{Li}^{'}$, the Frenkel disorder, Eq. (28), must be displaced toward the right to maintain equilibrium and an excess of $Li_I^{\cdot}$ over $V_{Li}^{'}$ will be built up. When this becomes sufficiently high, Li_3NbO_3 nucleates as a second phase.

These postulates raise one puzzling question. If cation place exchange and Li Frenkel defects, which include Li_{Nb} and $Li_I^{\cdot}$, form so easily, why is there no detectable Li_2O-rich single phase region?

$$3Li_2O \rightleftharpoons Li_{Li} + Li_{Nb}^{''''} + 3O_o + 4Li_I^{\cdot} \tag{29}$$
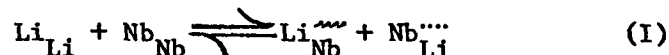
It is of interest to note that in the isomorphous $LiTaO_3$, single phase regions of comparable width have been reported for both sides of Li/Ta=1.000 (36).
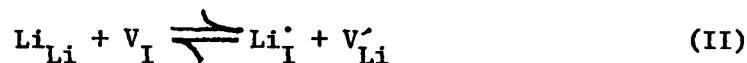
VI. SUMMARY OF THE DEFECT MODEL

The defect model for $LiNbO_3$ that results from this research program can be summarized as follows:

Undoped, stoichiometric $LiNbO_3$ is highly disordered by cation place exchange resulting in localized $LiNbO_3$ structure $\rightleftharpoons$ ilmenite structure disorder
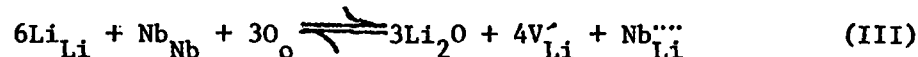
$$Li_{Li} + Nb_{Nb} \rightleftharpoons Li_{Nb}''' + Nb_{Li}'''' \qquad (I)$$

and by Li Frenkel disorder

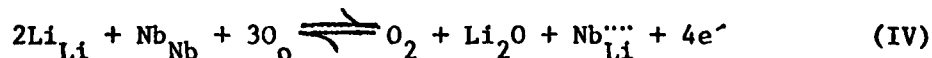$$Li_{Li} + V_I \rightleftharpoons Li_I^{\cdot} + V_{Li}' \qquad (II)$$

The resulting defect concentrations are comparable with those of the congruent composition, i.e. ~4 mole % V_{Li}' and ~1 mole % Nb_{Li}''''.

There is no significant region having a stoichiometric excess of Li_2O, but an extensive region of Li_2O-deficiency results in the loss of lattice sites in stoichiometric ratio, leaving excess Nb defects and V_{Li}'
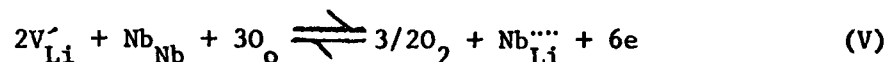
$$6Li_{Li} + Nb_{Nb} + 3O_o \rightleftharpoons 3Li_2O + 4V_{Li}' + Nb_{Li}'''' \qquad (III)$$

At the normally available congruent composition of 48.6 mole % Li_2O, the defect concentrations are 3.66 mole % V_{Li}' and 0.92 mole % Nb_{Li}''''. The increase in Li_2O-deficiency from the Li_2O-rich to the congruent has only a modest effect on the total defect concentrations because of the large amount of intrinsic disorder. Li_2O-loss beyond the congruent composition causes a significant increase in defect concentrations, but very quickly arrives at the $LiNbO_3$-$LiNb_3O_8$ phase boundary.

Reduction also causes the loss of lattice sites in stoichiometric ratio and the formation of Nb-excess defects. It is convenient to write a generalized reaction
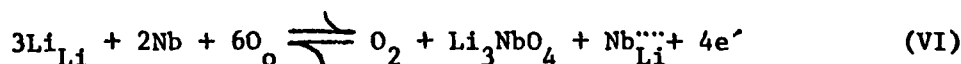
$$2Li_{Li} + Nb_{Nb} + 3O_o \rightleftharpoons O_2 + Li_2O + Nb_{Li}'''' + 4e' \qquad (IV)$$

If the crystal is already Li_2O-deficient according to Eq. III, the Li_2O generated by reduction can be accommodated by the reverse of the Li_2O-loss reaction, giving the net reduction reaction

$$2V_{Li}' + Nb_{Nb} + 3O_o \rightleftharpoons 3/2O_2 + Nb_{Li}^{····} + 6e \qquad (V)$$

As long as this does not disturb the defect concentrations that result from intrinsic disorder and Li_2O loss, the resulting electronic conductivity varies as $P_{O_2}^{-1/4}$. As reduction proceeds according to Eq. (V), the Li_2O activity in the crystal gradually increases. Reduction begins to have a pronounced effect on the defect concentrations and the Li_2O activity at about $P_{O_2} \sim 10^{-14}$ atm. For a congruent crystal reduced at 1050°C and 10^{-16} atm., [$Nb_{Li}^{····}$] will be increased by 1 mole %, and 2 mole % of V_{Li}' will be consumed, doubling the concentration of $Nb_{Li}^{····}$ and halving the concentration of V_{Li}'. According the Eq. (24), this will double the Li_2O activity in the crystal, which is then quickly driven to the Li_2O-rich phase boundary. Further reduction then ultimately results in nucleation and separation of Li_3NbO_4.

The Li_2O-rich composition is already saturated with Li_2O, so reduction according to Eq. (IV) immediately moves the crystal into the two phase region. Initially, however, the excess Li_2O can be accommodated by supersaturation according to the reverse of the Li_2O-loss equation, Eq. (III), with the V_{Li}' and $Nb_{Li}^{····}$ being available from the intrinsic disorder. The defect concentrations will not be significantly affected by reduction, however, until the extent of reduction approaches the level of the intrinsic disorder. The concentrations of $Li_I^·$ and $Li_{Nb}^{'''}$ will then build up rapidly and reach a sufficient degree of supersaturation to nucleate the second phase.

$$3Li_{Li} + 2Nb + 6O_o \rightleftharpoons O_2 + Li_3NbO_4 + Nb_{Li}^{····} + 4e' \qquad (VI)$$

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Since the defect concentrations due to intrinsic disorder and to Li_2O-deficiency at the congruent composition are similar, phase separation due to reduction should occur at about the same P_{O_2} for both Li_2O-rich and congruent (and even Li_2O-deficient) crystals, as observed.

Loss of Li_2O from the Li_2O-rich boundary to the congruent composition has only a modest effect on the electronic conductivity because the defect concentrations are controlled by intrinsic disorder over most of this range. The defect concentrations are significantly affected beyond the congruent composition, but the effect on the conductivity is still small, however, as predicted by the solution of the mass-action expression for reduction and the approximation to charge neutrality

$$n \approx (4K_{11})^{1/6}[V_{Li}]^{1/6}P_{O_2}^{-1/4} \qquad (VII)$$

The ionic conductivity at high P_{O_2} is due to V_{Li}' that result primarily from intrinsic disorder. It is affected by Li_2O-loss only at about the congruent composition and beyond. It should vary linearly with $[V_{Li}']$ and therefore much more strongly than the electronic conductivity. It would be necessary to carry the measurements to $P_{O_2} >> 1$ atm to verify that point. Since V_{Li}' are consumed by reduction, the ionic conductivity should decrease at very low P_{O_2}. The increased electronic conduction conceals any such effect, but the curvature of the transition between predominant electronic and ionic contributions is somewhat sharper than expected for an ideal shift from a dependence on $P_{O_2}^{-1/4}$ to no dependence on P_{O_2}.

The addition of even several percent of aliovalent impurities has very little effect on the defect chemistry, because this is barely enough to disturb the defect concentrations that result from intrinsic disorder. A slight increase in the diffusion constant of Ti in $LiNbO_3$ heavily doped

with MgO (10.7 mole %) is consistent with a proposed mechanism whereby Ti moves from one Nb site to the next by way of V'_{Li} (18). This should be a linear effect and therefore much larger than the effect of the dopant on electronic conduction.

The results of this study, and comparison with the work of Nagels (26), are consistent with electronic conduction by a small polaron mechanism with a thermally activated mobility

$$\mu_n = 6.33 \ T^{-3/2} \ e^{-0.49/kT} \ \frac{m^2}{v \ sec} \qquad \text{(VIII)}$$

In the temperature range used in this study, 900–1100°C, all of the electrons generated by reduction are equally free to contribute to conduction. According to the analysis of Nagels, the electrons are increasingly trapped below 500°C, so that in material equilibrated in air, the combination of exponential decrease in both mobility and carrier concentration leads to an insulating material at room temperature. Correction of the temperature dependence of conductivity with the temperature dependence of mobility yields an enthalpy of reduction reaction, Eq. (V) of 2.08 kj/mole per electron.

The analysis of the experimental results has been based on the classical mass-action approach that implies the validity of dilute solution thermodynamics in spite of the rather large defect concentrations. The accurate dependence of electronic conductivity on $P_{O_2}^{-1/4}$ indicates that this is valid at least for electrons. There has been no attempt to quantify the effects of ionic defects and there may be significant amounts of defect interaction and association that does not, however, detract from the general trends that have been discussed.

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VII. APPLICATION

The properties of $LiNbO_3$ important for electro-optic applications can be very sensitive to composition. Holman has shown, for example, that radiation damage is affected by the Li/Nb ratio, with the most Li_2O-deficient material being by far the most stable (16). One might have thought that the more defect-free Li_2O-rich material would have been the best. If the model of massive intrinsic disorder presented here is correct, then it is clear that Li_2O-deficiency will not significantly affect the defect concentrations until the Li_2O-deficient phase boundary is approached. So any difference would be expected only at or near that phase boundary. The total chemistry of the radiation damage is not understood. It seems clear that it starts with photoexcitation of an electron from an impurity, primarily Fe^{+2}, and that the electron migrates and is trapped elsewhere. "Elsewhere" has not been clearly identified. Fe^{+3} has been suggested frequently, but a combination of our work and the conduction mechanism studies of Nagels (26) suggests that a native defect could well be involved. The other side of radiation damage, of course, is the useful effect whereby phase holograms are formed by interference patterns such that information can be optically stored or processed. Proper control of this process requires knowledge of the photoexcitation and trapping phenomena.

The main current interest in $LiNbO_3$ involves the preparation of channel wave-guides that can serve as electro-optic switches to route light beams along any of several optional paths. These wave guides are traditionally made by thermal indiffusion of Ti strip patterns defined by photolithography. It is necessary to have uniform, reproducible indiffusion, and to avoid Li_2O outdiffusion that can result in a surface guide. A cooperative study of

the kinetics and mechanism of Ti indiffusion was undertaken with Bell Laboratories, Allentown, PA, in the form of the Ph.D. dissertation of Dr. Ronald J. Holmes, an outgrowth of this program. It was found that the diffusion constant increased slightly with increasing Li_2O-deficiency between the Li_2O-rich and congruent composition, and somewhat more rapidly as the Li_2O-deficient phase boundary was approached. In the meantime, the ferroelectric transition temperature decreases with increasing Li_2O-deficiency. Thus faster diffusion can be achieved in the ferroelectric phase at the Li_2O-rich composition because the slightly lower diffusion constant at that composition is more than compensated for by the higher available diffusion temperature (one does not want to exceed the transition temperature since the crystal would have to be repoled). This permits deeper diffusion in reasonable times to give the desired multimode operation. Previous practical diffusion depths were adequate only for single mode wave guides. Further work indicated that both the diffusion constant and the ferroelectric transition temperature were increased in the heavily Mg-doped $LiNbO_3$, giving a double further advantage. Multimode wave guides are of importance in the development of the submarine cable light wave system. This is an excellent example of interaction between basic science and practical application.

Dr. Holmes also confirmed that commercially available, as-grown "congruent" crystals can vary in composition by several tenths of a mole %. This is totally unacceptable for many applications. The obvious solution is to normalize the composition by equilibration to the Li_2O-rich phase boundary. This gives a reproducible, defined composition that permits deep Ti indiffusion and that is not metastable at low temperatures, as is the congruent composition.

Much of the discussion of defects in $LiNbO_3$ has been in terms of oxygen vacancies, based on the assumption that they are the major product of reduction. For example a very lengthy recent paper was devoted to theoretical calculations of energy levels associated with oxygen vacancies (30). As foreseen in the original proposal for this project, it has been shown that oxygen vacancies are not one of the major defects in $LiNbO_3$. In this regard, and with the defect model developed from this project, compositional effects in $LiNbO_3$ can be discussed on a more accurate basis.

VIII. FUTURE WORK

A. The most urgent item is to seek experimental support for the large amount of intrinsic disorder postulated in the proposed defect model. Several approaches are possible:

1. NMR studies have indicated that 6% of the Nb is in an abnormal crystalline environment in the congruent material. If this is due primarily to intrinsic disorder, the same result should be obtained for Li_2O-rich material.

2. The generation of large amounts of disorder will absorb significant amounts of enthalpy. A careful measurement of the heat capacity of Li_2O-rich $LiNbO_3$ (to avoid phase separation and resolution) up to about 1000°C could show an anomalous increase in heat capacity as the disorder effect becomes significant. This could be most easily done by differential thermal analysis.

3. Neutron diffraction has been used to disclose cation disorder in $FeTiO_3$, and might also be useful for $LiNbO_3$.

B. Anomalously high densities have been measured for reduced congruent crystals and for crystals equilibrated to the Li_2O-deficient phase boundaries. The fact that the measured densities of Li_2O-rich and congruent material agrees well with the crystallographic densities and the defect concentrations confirms the validity of the technique. In both cases the effect is seen just after the defect concentrations due to Li_2O-deficiency and to reduction exceed the proposed levels of intrinsic disorder. It is not clear how a crystal that maintains a filled oxygen sublattice can have an anomalously high density. For a start, the lattice parameters in this region should be rechecked.

C. Separation of a Li_2O-rich phase has been postulated for severely reduced congruent and Li_2O-deficient $LiNbO_3$. This should be confirmed by transmission electron microscopy and microanalysis.

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X. PERSONNEL

In addition to the Project Director, three postdoctoral Research

Associates have worked on this project:

Dr. Young Limb
    Ph.D. North Carolina State University
    Currently at Mostek, Inc.
    Colorado Springs,CO

Dr. Kwan-Wai Cheng
    Ph.D. MIT
    Initially with National Semiconductor, Palo Alto, CA. He has since
    returned to family business in Hong Kong

Dr. Young Ho Han
    Ph.D. Rutgers University
    Still employed in the Materials Research Center, Lehigh University

By subcontract from this grant, a collaborative effort was supported

with Professor Feigelson, Center for Materials Research, Stanford University,

leading to the preparation of highly doped single crystals of $LiNbO_3$.

Dr. Ronald J. Holmes, Member of the Technical Staff, Bell Telephone

Laboratories, Allentown, PA, carried out his doctoral dissertation on

"Diffusion of Titanium into Lithium Niobate" under the supervision of the

Program Director. Dr. Holmes' work was entirely supported by Bell Laboratories.

Dr. William Emkey, at that time a member of the physics faculty at the

Pennsylvania State University, Allentown Campus, assisted with the initial

experimental set-up as a Visiting Scientist for a period of six months.

Dr. Emkey is currently a Member of the Technical Staff, Bell Laboratories,

Allentown, PA.

XI. PRESENTATIONS AND PUBLICATIONS

A. PRESENTATIONS

1. D. M. Smyth, "Defect Chemistry of $LiNbO_3$", a seminar, Bell
   Laboratories, Allentown, PA, December 3, 1981.

2. D. M. Smyth, "Defects and Transport in $LiNbO_3$", a seminar, Battelle Columbus Laboratories, Columbus, OH, January 21, 1983.

3. Y. Limb and D. M. Smyth, "Oxygen Nonstoichiometry and the Li/Nb Ratio in $LiNbO_3$", Joint Session on Single Crystals and Directionally Solidified Materials: Preparation and Properties, American Ceramic Society, Washington, DC, May 5, 1981.

4. Y. Limb, K. W. Cheng, and D. M. Smyth, "Composition and Electrical Properties in $LiNbO_3$", A poster presentation, Fifth International Meeting on Ferroelectricity, The Pennsylvania State University, August 18, 1981.

5. R. J. Holmes and D. M. Smyth, "Diffusion of Ti into $LiNbO_3$ Crystals of Different Compositions at 1050°C", Electronics Division, American Ceramic Society, Cambridge, Mass., September 14, 1982.

To be delivered:

6. D. M. Smyth, "Defects and Transport in $LiNbO_3$", an invited paper, 1983 IEEE International Symposium on Applications of Ferroelectrics, NBS-Gaithersburg, MD, June 1-3, 1983.

7. R. J. Holmes, Y. S. Kim, D. Smyth, and C. D. Brandle, Jr., "Evaluation of Crystals of Lithium Niobate Doped with MgO or TiO_2 for Waveguiding Applications", 1983 IEEE International Symposium on Applications of Ferroelectrics, NBS-Gaithersburg, MD, June 1-3, 1983.

B. PUBLICATIONS

1. Y. Limb, K. W. Cheng, and D. M. Smyth, "Composition and Electrical Properties in $LiNbO_3$", Ferroelectrics <u>38</u>, 813 (1981).

To appear:

2. D. M. Smyth, "Defects and Transport in $LiNbO_3$", Proceedings of the 1983 IEEE International Symposium on Applications of Ferroelectrics.

3. R. J. Holmes, Y. S. Kim, D. Smyth, and C. D. Brandle, Jr., "Evaluation of Crystals of Lithium Niobate Doped with MgO and TiO_2 for Waveguide Applications", Proceedings of the 1983 IEEE International Symposium on Applications of Ferroelectrics.

In preparation:

4&5. Two papers with R. J. Holmes on the kinetics and mechanism of titanium diffusion in $LiNbO_3$.

6&7. Two papers on the defect chemistry of $LiNbO_3$ based on the results and model described in this report.

35.

XII. TRAVEL

Funds from this grant made possible visits to five solid state laboratories in Western Europe in August, 1980. This was an outstanding opportunity to become acquainted with the current work of some of the leading research groups in this field. These visits and the personal contacts that results, have been of lasting benefit. The laboratories and main people involved included:

> University of Oslo, Norway
>   Professor Per Kofstad
>   Department of Chemistry
>
> State University Utrecht, The Netherlands
>   Professors, Geno, Broers and deWit
>   Department of Inorganic Chemistry, and
>   Blasse and Schoonman
>   Solid State Department of the Physical Laboratory
>
> Technical University of Hannover, West Germany
>   Professors Dieckmann, Haul, and Göpel
>   Institüt für Physikalische Chemie
>
> Philips Forschungslaboratorium, Aachen, West Germany
>   Drs. Härdtl, Wernicke, Hagemann, Irhig
>
> Fraunhofer Gesellschaft, Freiburg, West Germany
>   Drs. Räuber, Dischler, Feisst, and Schirmer

XIII. FIGURE CAPTIONS

1. Equilibrium electrical conductivity of $LiNbO_3$ as reported by Bergmann (22) and by Jorgensen and Bartlett (23).

2. Equilibrium conductivity of $LiNbO_3$ of congruent composition at 50° intervals from 950°-1100°C.

3. Isobaric Arrhenius plots of the electrical conductivity of $LiNbO_3$ of congruent composition.

4. Equilibrium electrical conductivity of $LiNbO_3$ at 1050°C for the congruent composition and for crystals equilibrated to the Li_2O-deficient, and Li_2O-rich phase boundaries.

5. Isothermal cross-section of a schematic phase diagram for $LiNbO_3$. D, C, and R refer to the Li_2O-deficient, congruent, and Li_2O-rich compositions.

6. Cation stacking sequences along the "hexagonal" axis for the corundum, ilmenite, and $LiNbO_3$ structures. Taken from Wells (31).
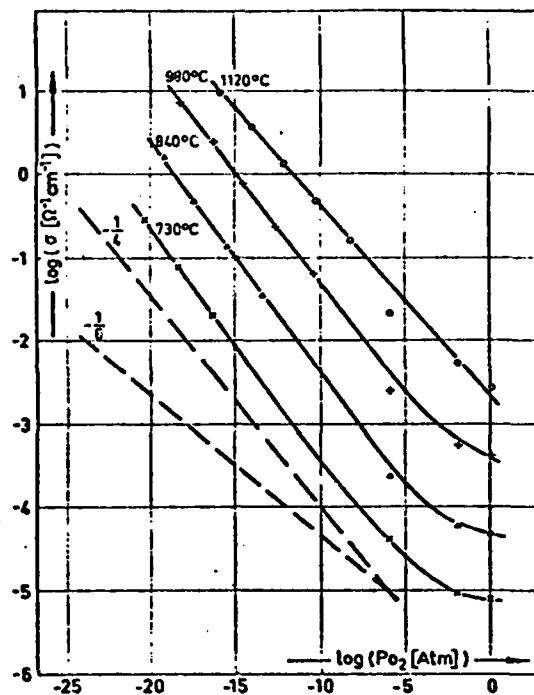
FIG. 2

Electrical conductivity $\sigma_\perp c$ of
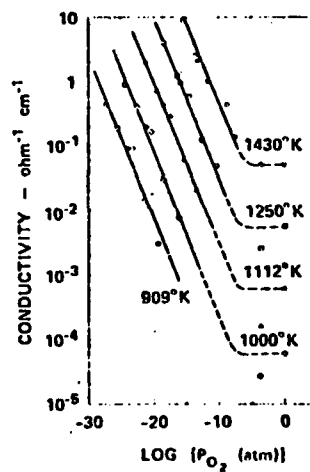LiNbO$_3$ as a function of oxygen
partial pressure for various
temperatures.

Bergmann (22)

Fig. 4. Isothermal plot of the electrical conductivity of
LiNbO$_3$ as a function of the partial pressure of oxygen.
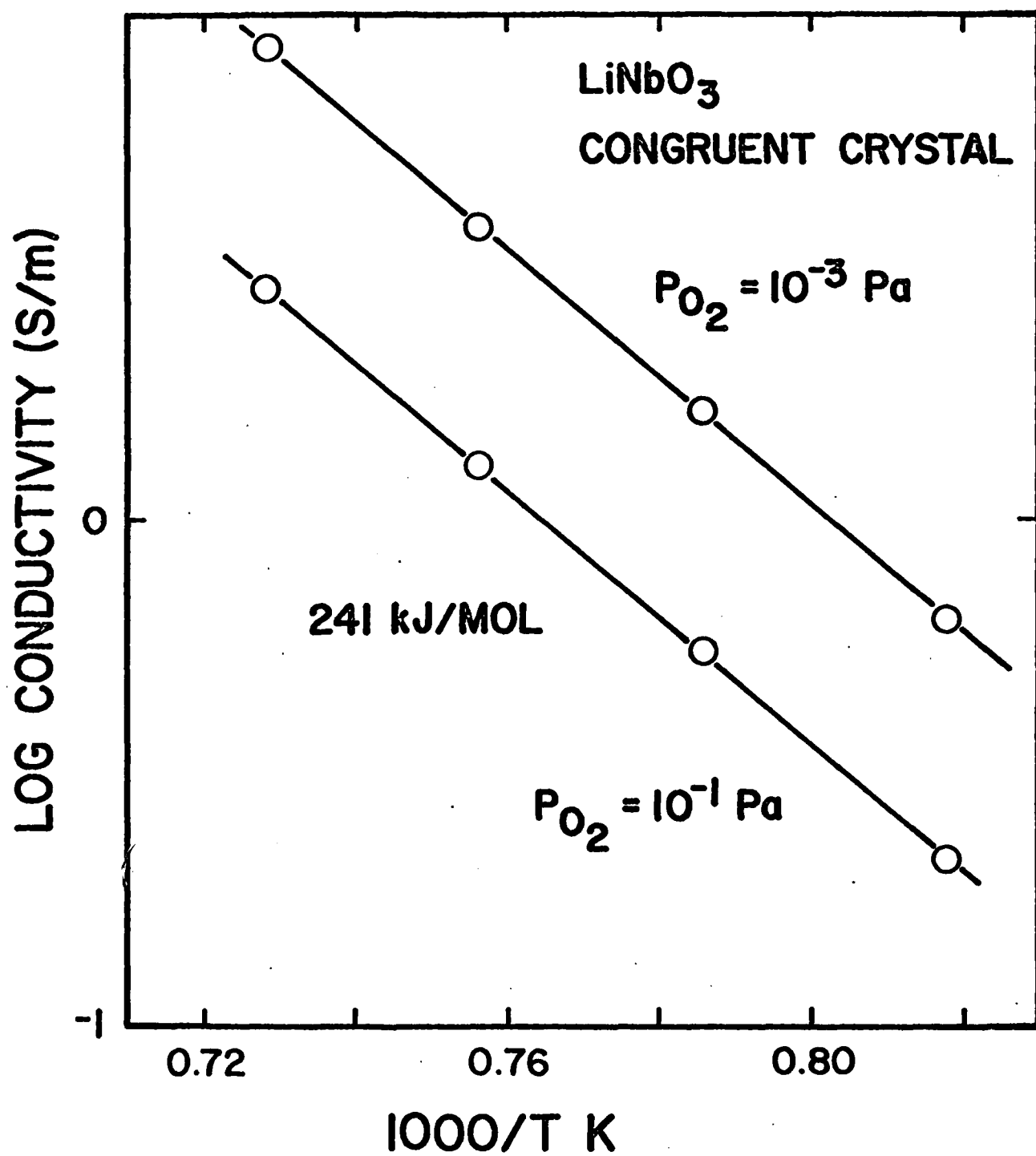
Jorgensen and Bartlett (23)

Figure 1

38.

Figure 2
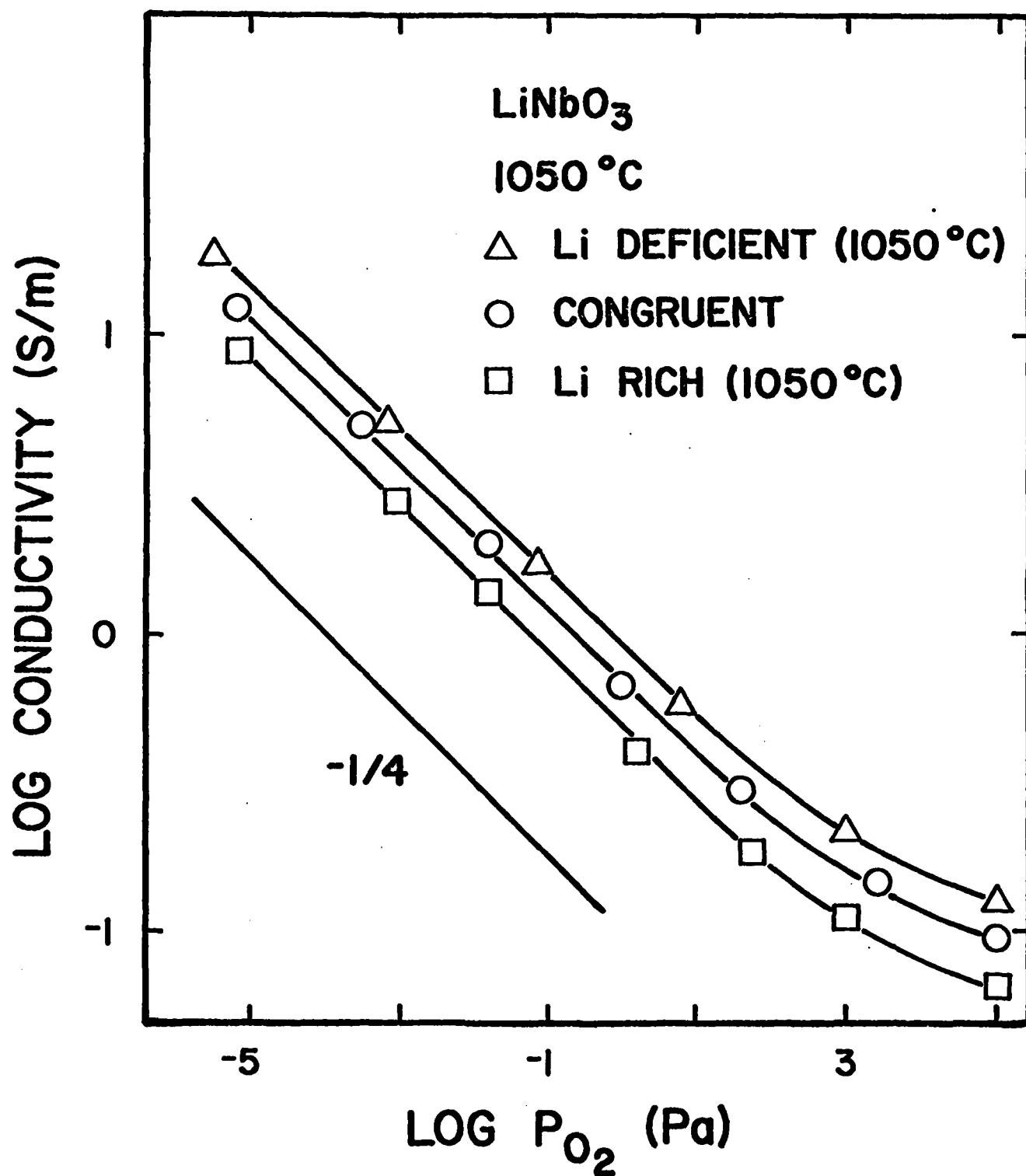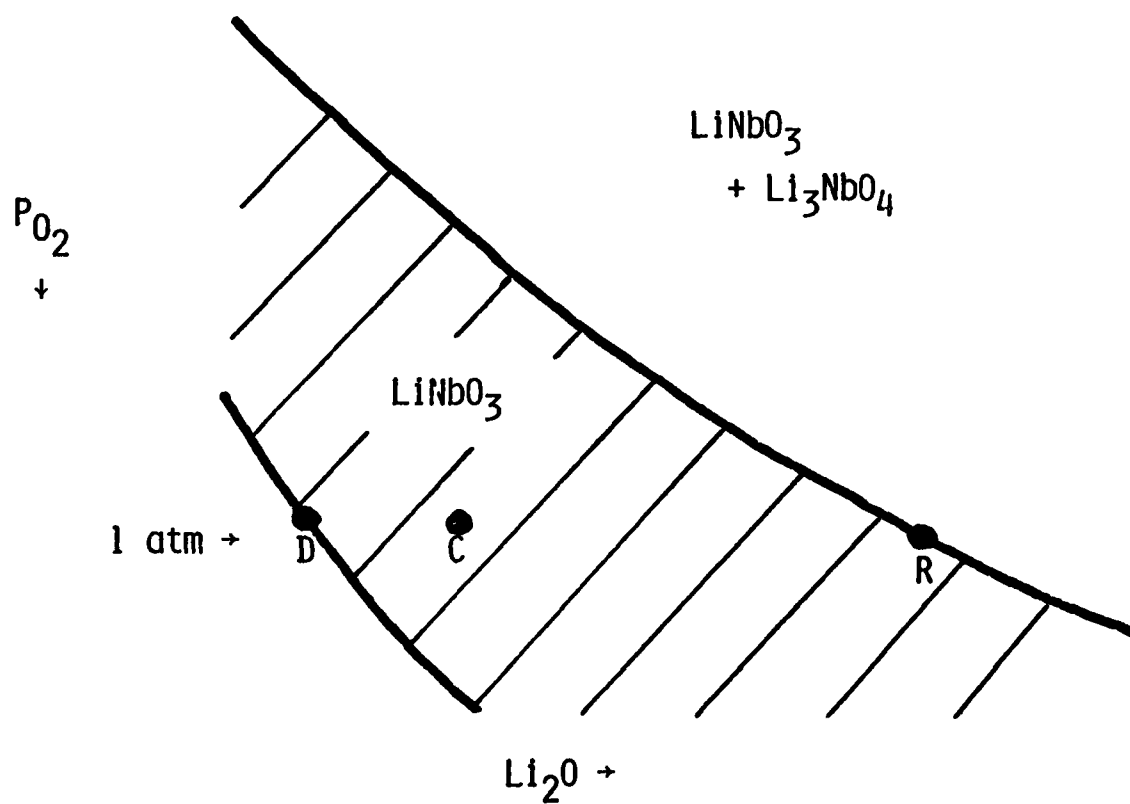
39.

Figure 3

Figure 4

41.

Figure 5

42.

O = Al   O = Fc   ● = Ti   O = Li   ● = Nb

z-Al₂O₃   FeTiO₃   LiNbO₃

(a)   (b)   (c)

Figure 6

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